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EXPERIMENTAL INVESTIGATION OF THE SLOW OXIDATION OF HYDROGEN AND THE THIRD IGNITION LIMIT

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Introduction

A detailed analysis of published experimental data relative to the dependence of kinetics of slow oxidation of hydrogen and location of the third limit of ignition with reference to the initial pressure, temperature, treatment of the reaction vessel, etc., was made by Voyevodskiy in 1946 (1). In this review, he showed that the nature of the processing of a reaction vessel can have an effect on the mechanism of ignition at the third limit.

In the case where the probability of the recombination of the HO_2 radical -- the carrier of the chain -- upon touching the container wall is small (the case of untreated vessels), the reaction has an autocatalytic character, the liberation of heat promotes the acceleration of the reaction, and the explosion has a purely thermal character. In a vessel treated with KCL (or other salts), the rate of the heterogeneous reaction of HO_2 radicals on the container wall is great and the rate of oxidation becomes small. Ignition, however, does occur at a pressure not much greater than that in the clean vessel and at the same temperature. This phenomenon, as well as the relationship of the induction period to the initial pressure, permitted the conclusion that in this case ignition is dependent on the occurrence of branched reaction chains rather than liberation of heat.

The equations derived for this case (1) were confirmed as highly accurate (2), by taking into consideration the later data of Willbourn and Hinshelwood (3).

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All studies in which the transition of a slow reaction into ignition was investigated, have been conducted in vessels treated with salts because the results are more easily reproducible in such containers. In order to include all possible cases, this paper considers the problems concerned with the relationship between the kinetics of the slow reaction and ignition in clear vessels treated with KCl.

Experimental Procedure

Pyrex and quartz spherical vessels with a diameter of 4 centimeters were used; the clean containers were washed with cold concentrated HNO_3 and distilled water, and the vessels treated with KCl were washed with an aqueous solution of KCl.

Hydrogen was introduced first into the heated reaction vessel (at a pressure higher than the second limit), and then the oxygen was introduced, after which either the ensuing flash was observed or the kinetics as shown by the decrease in pressure were determined (a mercury manometer with an accuracy of about one millimeter Hg was used). When the mixture contained water vapor, it was introduced first, and hydrogen and oxygen were filled in afterwards. The temperature of the furnace was measured by an iron-constantan thermocouple with an accuracy of about one degree.

The gases were prepared electrolytically, and all of the experiments were conducted with stoichiometric mixtures. The time taken to introduce the oxygen was always 4 seconds., this being made possible by the use of a sufficiently accurate capillary tube. Because of the long induction period, it can be assumed that complete mixing with the oxygen was accomplished at this rate of feeding.

To check the data obtained by using the above procedure, experiments were also conducted with quartz vessels filled with the mixture and immersed in a constant temperature bath containing molten tin. A flash indicated the transition into the field of ignition at increased pressure or temperature. The results obtained by the two methods checked.

Nature of the Kinetics and Location of the Ignition Limit

At each temperature point considered, several experiments were conducted at various pressure with both types of containers in order to determine the nature of the kinetics, the values of p_3, and the dependence of the induction period of ignition on the pressure. Data on the measurement of the limit are presented in Table 1 and in Figure 1. (The graph whose coordinates are P and T_3 shows that a smooth curve can be drawn separating the area in which ignition occurs from the area under the limit in which ignition does not occur.)

The induction period of ignition (the values for which are depicted parenthetically in seconds in Table 1) for both types of containers is decreased along with a pressure increase at a given temperature, but its value is smaller at the ignition limit, in a higher temperature range.

Kinetics of the reaction under the limit and during the induction period of ignition depend on the nature of the container walls (see Figures 2 and 3). In the clean vessel, in conformity with N. M. Chirkov's data (4), the reaction kinetics have an autocatalytic character, and the induction period of ignition is determined by the time consumed in reaching a rate where the input of heat is equal to the output of heat.

In a vessel covered with KCl, the reaction velocity is approximately 3-4 times less than the maximum velocity in pure vessels at a similar distance from the limit (although P and T are higher here), and maintains a constant value up to the slowing down of the reaction through combustion. The kinetics during

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the induction period of ignition have such a character that the pressure falls at a constant rate and no marked change in the velocity occurs before the flash. This fact proves the accuracy of the concept concerning the chain character of ignition in this case. The conversion of hydrogen into water at a constant rate in the period of induction causes, in the last analysis, a disturbance of the stationary condition underlying the chain reaction's course.

Qualitative Experiments Confirming the Major Role of Active Intermediate Products in Slow Oxidation

In order to confirm the conclusion that there is a considerable concentration of an active intermediate product present in this reaction (which these authors assume to be the radical HO_2), two series of qualitative experiments were conducted, employing a new procedure developed by N. N. Semenov and N. M. Emanuel' (5).

The first series was conducted in clean Pyrex vessels containing a mixture of H_2 and O_2 which had been introduced in the same order as before, this time at a pressure close to 60 millimeters Hg below the ignition limit. After 10-15 seconds, when the pressure had dropped by 5-6 millimeters, a fresh mixture was added to the vessel and the position of the limit was determined. If it is assumed that the reaction leads only to the formation of water, then during this time 10-12 millimeters Hg of water should have formed. The ignition limit obtained in this manner lies below the limit for the dry mixture and also below the limit for a corresponding mixture containing added water.

Data from this series are presented in Table 2, and are also depicted in curve IV of Figure 1, where p represents the partial pressures of a stoichiometric mixture (the total pressure reduced by 10 millimeters Hg). In the authors' opinion, these experiments show that active intermediate substances which are capable of vigorously catalyzing the reaction in the fresh mixture are formed in the initial stage.

The second series was carried out in clean quartz vessels. After determination of the induction period under the given conditions, experiments with "quenching" were conducted. In the course of the induction period, the vessel was removed from the constant temperature bath. After cooling in the air, the vessel was once more placed in the constant temperature bath, and a flash resulted.

The induction period remains the same as in the absence of quenching. These results show that after elimination by cooling of the active intermediate products, induction of the reaction requires practically the same time as with a fresh mixture. These experiments also confirm the thermal nature of ignition in clean vessels. In order that an explosion take place here, the presence of a definite concentration of stable molecules is not necessary, as in the case of a chain explosion. The factor which determines the occurrence of an explosion in the conditions under consideration is attainment of a definite value of the rate of heat formation due to a high concentration of intermediate active products.

Conclusion

1. The reaction kinetics and also position and nature of the ignition limit are essentially dependent on the nature of the container wall. In clean vessels, as shown earlier by Chirkov (4), the reaction has an autocatalytic character and the ignition has a thermal nature.

The temperature curve is determined by the factor $e^{\frac{25000}{RT}}$.

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In vessels treated with KCl, the reaction rate remains practically constant both under the limit and also during the course of the induction period of ignition, which in this case has a clearly pronounced chain character. The temperature relationship of the limit is determined by the factor $e^{\frac{36000}{-RT}}$.

2. All mechanisms investigated (the dependence of the ignition limit on the temperature and the addition of water; the dependence of the induction period of ignition on the initial pressure) are quantitatively described by the standard mechanism for the oxidation of hydrogen.

3. Calculations more accurately defined the values for the constants of the rates of the processes:

$$HO_2 + H_2 = H_2O_2 + H \text{ and } HO_2 + H_2O = H_2O_2 + OH$$
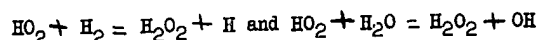
which are equal, respectively, to:

$$1.7 \times 10^{-13} e^{-\frac{24000}{RT}} \text{ and } 2 \times 10^{-16} e^{-\frac{8000}{RT}} \quad \frac{cm^3}{sec}$$

The value for the energy of activation of the process for the origination of the chains, $H_2 + O_2 = 2OH$, was approximately determined as $E_o = 49,000$ calories/mol.

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/Figures and tables follow/

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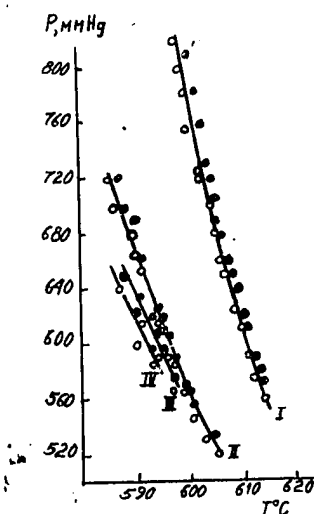CONFIDENTIAL

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Figure 1. Dependence of the Ignition Limit on the Temperature.

I- experiments in vessels treated with KCl; II- experiments in a clean Pyrex vessel; III- experiments with mixtures containing 2 percent H_2O in a clean vessel; IV- experiments with impurities in the mixture during the reaction.

●-values of p^+ : o - values of p-
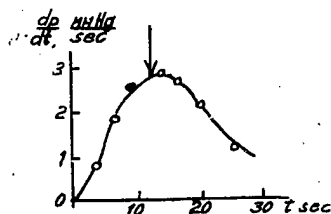

Figure 2. Kinetics Under the Limit and During the Induction Period in a Clean Pyrex Vessel. Two experiments at $T = 597°C$; ● - p = 585 millimeters Hg (flash not occurring, the maximum rate attained in 15 seconds); ● - p = 590 millimeters Hg (flash at 12 seconds.)
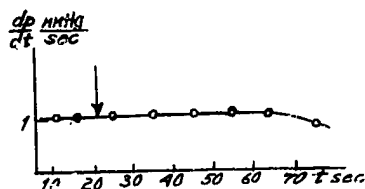

Figure 3. Kinetics Under the Limit and During the Induction Period in a Pyrex Vessel Washed with KCl Solution. Two experiments at $T = 607°C$: o - p = 650 millimeters Hg (flash not occurring, rate having a constant value); ● - p = 660 millimeters Hg (rate having the same value, flash occurring at 21 seconds.)

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Table 1

Clean Pyrex Vessel

T°C	585	586	587	588	589	590	590	591	593	594	594
p+, mm Hg			720(20)	700(23)	(700)21	690(25)	700(20)	660(21) 655	620	624(14) 615	645(8)
p-, mm Hg	720	700		640	680	665					

T°C	595	596	597	597	599	599	600	601	602	603	605
p+, mm Hg	618(19)	605(16)	590(12)	600(8)	570(12)	580(7)	565(10)	555(8) 545	570(5)		535(4) 520
p-, mm Hg	610	590	585		565					530	520

Clean Pyrex vessel; a mixture containing 2% H_2O relative to the total pressure (in the table below are given the partial pressures of the stoichiometric mixture).

T°C	591	594	595	597
p+, mm Hg	635(2)	604(8)	595(10)	575(10) 565
p-, mm Hg	615	590		

Quartz and Pyrex vessels treated with KCl (in the quartz vessel the second procedure was used to obtain the values denoted).

T°C	598	599	602	604	605	605	606	606	607	607
p+, min Hg		810(15)"	760(25)"	720(30)	690(26)	700(21)	680(36)	720(3)	660(21)" 650	670(14)
p-, mm Hg	800"	756"	720	700	670"	680				

T°C	608	609	610	610	611	612	613	614	614	614
p+, mm Hg	655(18)	640(21)	620(20)	700(2)	610(8)	590(12)	600(8)	580(6)	570(5) 560	600(3)
p-, mm Hg	625		600		590	575				

Quartz vessel treated with KCl, a mixture containing 2% H_2O relative to the total pressure (experiments conducted according to the second procedure)

T°C	597	599	601	602	603	604	605
p+, mm Hg			784(24)		731(23)	707(16)	704(15)
p-, mm Hg	820	782		724		700	680

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Table 2

$T°C$	Pressure at Which Mixture Is Formed	p^+	p^-
587	630		640
588	630	640(4)	
589	600		690
590	600	625(8)	
593	560	695(6)	585

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